

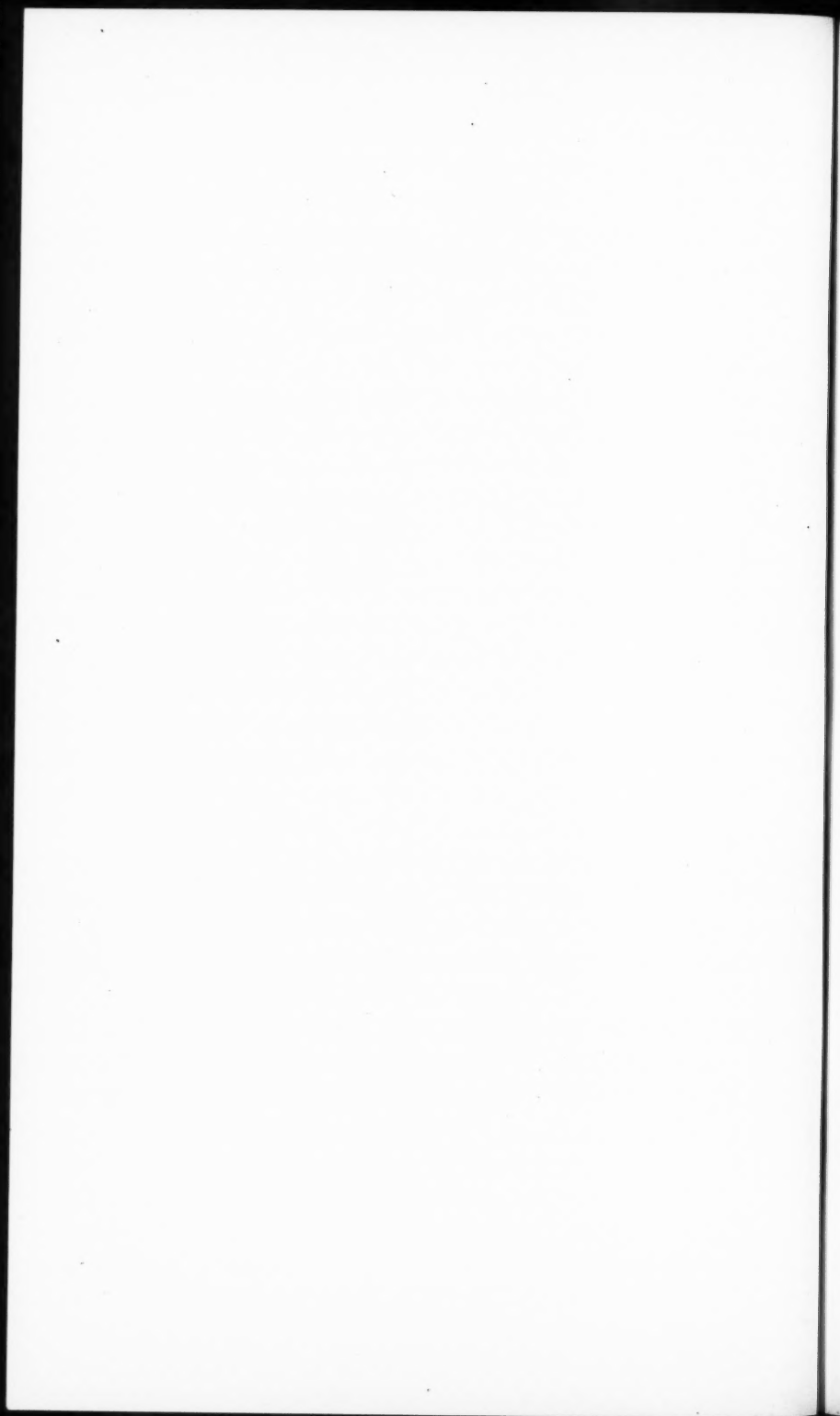
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ROUGH COMPRESSIBILITIES OF FOURTEEN
SUBSTANCES TO 45,000 Kg/Cm²

By P. W. BRIDGMAN

INVESTIGATIONS ON LIGHT AND HEAT MADE WITH AID FROM THE RUMFORD FUND



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INTRODUCTION

In two preceding papers¹ the parameters of a number of transitions have been determined up to 45,000 kg/cm². The method consists in determining at various temperatures the discontinuity in volume by measuring the displacement of the piston by which pressure is produced. If instead of determining the discontinuity in the motion of the piston, one plots the motion of the piston at constant temperature as a function of pressure, one obviously has a rough measure of the compressibility. Various corrections, however, reduce the accuracy of the method and restrict its applicability to the more compressible substances. It probably will be possible to improve the method, and in fact I now have under construction an apparatus which should permit better values. But in the meantime, because of their intrinsic interest, I give in the following pages rough results for some of the more compressible substances, for which the results should be most accurate.

TECHNIQUE AND CORRECTIONS

If the contents of a cylindrical container are subjected to pressure by the thrust of a piston, the total displacement of the piston is evidently determined by the compression of the contents, the distortion of the container, and the distortion of the piston and packings. If the contents possess much mechanical stiffness, then friction on the walls produces a stress system in the contents which is not a hydrostatic pressure, and the interpretation of the piston displacement is not clear. The first requirement, therefore, is to make the pressure approximately hydrostatic. This was accomplished by enclosing the material under measurement in a lead sheath. The general arrangements are indicated in Figure 1, drawn to scale. They are practically the same as for the transition measurements. In the previous paper a discussion was given of the distortion of the container under pressure adequate for the purposes of that paper, but here the requirements are more exacting, and a more elaborate examination is necessary. Suppose, for example, that an incompressible substance is compressed in a cylinder to such a pressure that the increase of cross section of the container is 10 per cent. If now a transition occurs, and the change of volume is measured by measuring the displacement of the piston, a 10 per cent error will be made in the ΔV of the transition if no correction is made for the change of cross section. But on the other hand, before the transition occurs a 10 per cent compression would have been ascribed to the substance if no correction had been made for the cross section, whereas the actual compression was zero. That is, an infinite error in the compression against a 10 per cent error in the volume change of the transition is here the result of improperly correcting for the distortion of the container.

An exact evaluation of the corrections is out of the question. Not only are the boundary conditions incapable of exact formulation, but the stresses are beyond the range in which linearity holds between stress and strain, and there is marked hysteresis. The latter effect should be approximately eliminated by using the mean of measurements with increasing and decreasing pressure. The elastic deformation was dealt with by computing it for idealized conditions, and then manipulating the results to secure agreement with certain check measurements. The idealized elastic problem is that of the infinitely long cylinder under external and internal hydrostatic pressure, the inner and outer radii being taken as those at mean positions along the axis of the cone. The external pressure can be evaluated, as explained in the previous paper, from measurements of the longitudinal

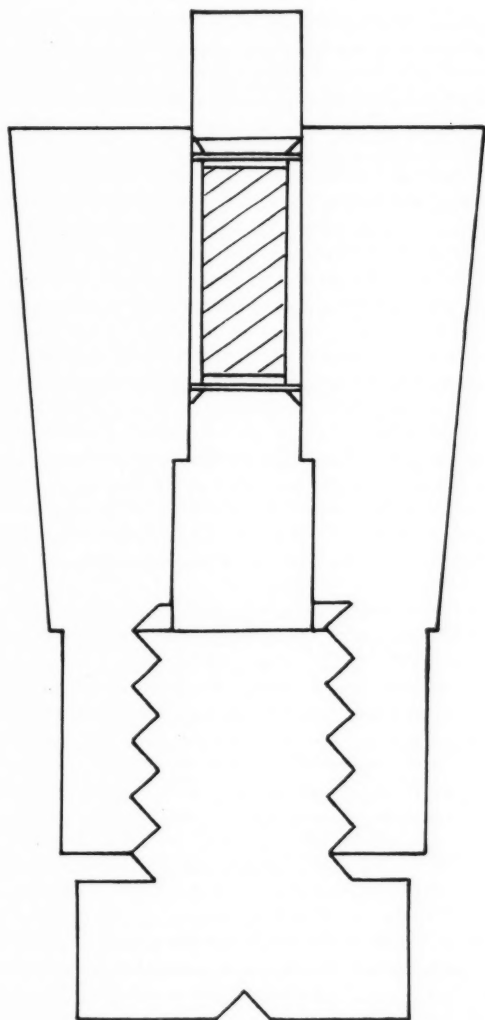


FIGURE 1. Shows the method of mounting the specimen (cross hatched) in a lead sheath for compressibility measurements.

displacement of the cone into the sleeve, which gives the means for evaluating the friction. The idealized infinite cylinder fails to correspond to the actual case not only because of the conical figure of the actual container, but also because of the closures at the ends, one end carrying the freely moving plunger and the other end being closed by a screw plug which transmits a longitudinal tension to the walls of the container. On the outside of the container there is a longitudinal shearing force which gets transformed into a mean longitudinal tension inside. The distortion of an infinite cylinder under longitudinal tension can be calculated, and crude allowance made for these effects. Then there is the very important effect of finite length; the length of the cavity was on the average 2.5 times the diameter. This means that very effective support is afforded by the ends, which are not exposed to the internal pressure, although exposed to external pressure. As a result the cavity must become somewhat barrel shaped, and the cross section at the piston is different from that at the center of the cavity. In an infinite cylinder a simple application of Betti's theorem shows that the increase of cross section at the piston is only one half as great as that further down in the cavity. This means that the effective correction of the cross section that is to be used for computing the pressure from the thrust on the piston is of the order of only one half the correction on the cross section from which the total change of volume is to be computed.

There are two independent measurements that can be made to check any computations. The longitudinal displacement of the container into the collar can be measured as a function of the thrust on the piston, and the internal change of volume can be measured when there is no internal pressure but the external pressure is made to be approximately the same as in the actual experiment by exerting on the whole container the same total thrust as that which in the actual experiment is exerted on the piston. This latter change of internal volume was measured by sealing a graduated capillary into the cylinder, which was filled with mercury, and observing the motion of the mercury column in the capillary as a function of thrust. The longitudinal displacement into the collar agreed exactly with that computed. The change of internal volume was 0.8 of that calculated for the infinite cylinder; the difference is to be ascribed to the effects due to the unknown distribution of longitudinal stress, departure from cylindrical figure, etc. The calculated corrections for the effect of internal and external pressure together were therefore reduced by this factor of 0.8. An additional reduction factor of 0.9 was guessed

at to allow for the difference of terminal conditions in the two cases, making a total reduction factor on the correction calculated for the infinite cylinder of 0.7. The final correction assumed for the maximum pressure (50,000 kg/cm²) was 2.7 per cent on the effective area from which the compression was calculated, and 1.5 per cent on the area from which pressure was calculated. These corrections were taken to be linear with pressure.

As actually used, this was a differential method, similar to that which I had used to measure the compressibility of liquids,² and which has been extensively used at the Geophysical Laboratory in Washington in measuring the compressibility of solids.³ The cylinder was filled with the substance under investigation in its lead sheath, and the displacement of the piston determined as a function of pressure. This was done on a careful time schedule. Pressure was first increased to the maximum in steps of 10,000 at intervals of 1 minute, released to 0 and again increased to the maximum on the same time schedule. This constituted the preliminary seasoning. Pressure was now released to 0 and increased back to the maximum in steps of 2,000 on a 1 minute schedule. This run down and up in 25 steps each way and in 50 minutes altogether constituted the essential part of the measurements. Pressure was finally reduced to 0 in 10,000 steps on the 1 minute schedule and the apparatus taken apart. It was now set up again with a core of soft steel replacing the previous substance, in a lead sheath of approximately the same size as at first. The same sequence of measurements was now made on the lead and steel. Next the differences of corresponding displacements of the two runs were computed, plotted on large size paper, and a single curve drawn as the mean of ascending and descending branches. A detailed discussion of the effects of friction, which I will not take space to give here, showed that it is better to take the differences of ascending and descending branches of the two curves, and then draw the mean curve of the loop thus obtained, rather than to draw the mean curves for the two loops and then take the difference of the mean curves.

The upper end of the loops require somewhat special treatment. Figure 2 shows how the top of the loop runs horizontally on release of pressure during an interval corresponding to the friction on the piston. In taking the mean loop, this frictional effect was eliminated as best it might by extrapolating the curve AC beyond C graphically, and using the mean of this extrapolated curve and AB in the pressure interval CB.

The maximum pressure listed in the following is 45,000 kg/cm²,

corresponding roughly to the mean between the pressures at C and at B. The maximum pressure on the piston was more than 50,000, but friction reduced this in the material under measurement. It would have been easy to extrapolate from the results to an effective maximum pressure of 50,000, but there is no reason why the reader should not make this extrapolation to suit himself.

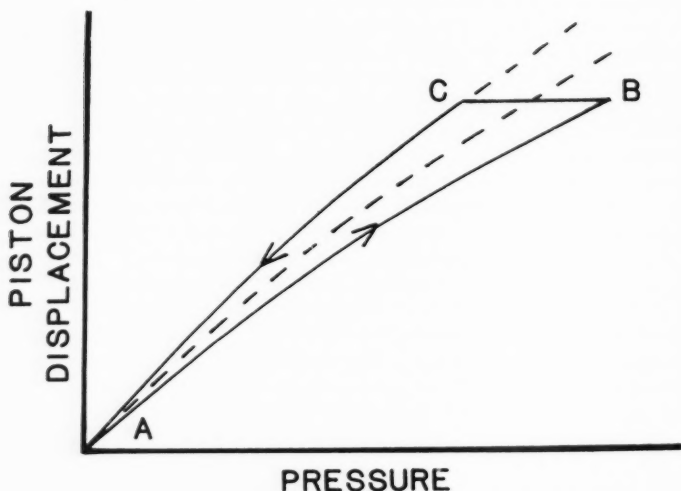


FIGURE 2. Idealized plot of piston displacement against pressure.

The final result was a smooth curve corresponding to the difference of compressibility between the substance under investigation and iron. Since the compressibility of iron is small compared with that of the other substance, I assumed for the compressibility of iron values extrapolated from my previous measurements to 12,000. I had formerly found by direct measurement up to 12,000 at 30° for the compressibility of iron:

$$-\Delta V/V_0 = 5.87 \times 10^{-7} p - 2.37 \times 10^{-12} p^2,$$

p in kg/cm². Since in the following all quantities of material were determined by weighing, what is needed is the compression of iron in cm³ per gm. The following were assumed to be the compressions in cm³ of 1 gm of iron at pressures of 10,000, 20,000, 30,000, 40,000, and

50,000 kg/cm² respectively: 0.00072, 0.00137, 0.00196, 0.00250, and 0.00298.

Since it was not usually convenient to use exactly the same amounts of lead in the actual and the blank runs, the compression of the differential amount of lead also entered as a correction. The compression of lead to 45,000 was determined by direct measurement by filling the container entirely with lead. The following are the values found for the compression in cm³ per gm at 10,000, 20,000, 30,000, 40,000, and 50,000 respectively: 0.0020, 0.0036, 0.0051, 0.00635, and 0.0075. The previous measurements up to 12,000 could be reproduced by a second degree formula. The previous measurements were 0.0019 at 10,000 and 0.0035 extrapolated to 20,000. The agreement is not bad. Beyond 20,000 the second degree formula representing the former results goes off badly, at 50,000 giving a change of volume of 0.0060 against 0.0075 experimental. The change of volume thus actually proceeds at a more rapid rate than the second degree formula would indicate. This is as is to be expected, because the second degree formula demands a minimum compression and a reversal at very high pressures.

The useful life of one of the containers was rarely as much as ten applications of the maximum pressure. In the transition measurements 20 applications were not unusual. The conditions here were more exacting, however, and much closer track was kept of the progress of permanent distortion. A special arrangement was made for measuring the internal diameter of the container at different points along the axis to an accuracy of 0.0001 inch, and after every completed run the container was remeasured for permanent distortion, and discarded, or else reamed to a slightly larger size, when the permanent stretch got as high as 0.002 inch, which experience showed to be about the maximum tolerable. It would have been very convenient if it had been possible to make the blank runs on iron and lead on a single container once and for all, but this did not prove to be possible, since the containers were not sufficiently reproducible. This made it necessary to make a blank run with each new container. On the average a container yielded results for the compression of only one substance. If it had been possible to get reproducible containers, results could have been obtained twice as fast and with twice as great an economy in containers.

A great deal of preliminary work was put into getting the best details of the various manipulations, such as the time schedules etc., to give most reproducible results. In the preliminary work a good

many measurements were made on the same substance, but after the method was established, one or two set-ups usually sufficed. A check on the accuracy of the measurements is afforded by comparing with the results previously obtained up to 12,000 and in some cases to 20,000. The low pressure end of the range was in general much less accurate than the high pressure end; in many cases the results were adjusted so as to agree with previous results over the first 5,000 kg/cm².

The detailed results now follow.

DETAILED RESULTS

Lithium. One set-up was made for this substance, with the corresponding blank run. In Table I is given the compression at room

TABLE I
COMPRESSION OF THE ALKALI METALS

Pressure kg/cm ²	Compressions				
	Lithium cm ³ /0.534gm	Sodium cm ³ /0.971gm	Potassium cm ³ /0.870gm	Rubidium cm ³ /1.532gm	Caesium cm ³ /1.88 gm
5,000	.043	.071	.116	.164	0.182
10,000	.074	.117	.183	.233	.271
15,000	.101	.148	.230	.279	.326
20,000	.125	.182	.268	.316	.372
23,000					{ .398
					{ .404*
25,000	.145	.209	.301	.345	.420
30,000	.165	.233	.329	.371	.438
35,000	.184	.254	.353	.393	.464
40,000	.202	.273	.375	.413	.487
45,000	.218	.290	.396	.431	.507

* Phase change

temperature of that amount of material which occupies 1 cm³ under normal conditions. Some check on the results can be obtained by comparison with previous measurements up to 20,000.⁴ Previous measurements of the compression at 10,000 and 20,000 were 0.073 and 0.123 against 0.074 and 0.130 found now.

Sodium. Three different set-ups were made with three corresponding blank runs. One of the blanks was made with lead and gold instead of lead and iron, the idea being that gold might be so much softer than iron as to result in the pressure being appreciably more hydrostatic throughout the container, but no superiority of this run was found over that with iron, and gold was not tried in other blanks.

There was no consistent difference between the results of the three runs; the one which gave the lowest compression at 20,000 gave the highest at 45,000. The results are given in Table I. The low pressure results were adjusted to agree with the former ones⁵ at 10,000. At 20,000 the change of volume now found is 0.183 against 0.189 found before. The direction of deviation is the same as for lithium. The former results are doubtless to be preferred. I do not think, however, that this means necessarily an error in the same direction at the highest pressures of the range, but I think it probable that the effect is connected with hysteresis, and that the maximum error might be looked for at the center of the range. This would mean that the relation found in all the work described in this paper between pressure and change of volume is probably a little too nearly linear, the actual compressibility dropping more rapidly at high pressures than found here.

Potassium. One set-up was made, but runs were made at three temperatures: room temperature, 75°, and 125°, in an attempt to find the temperature coefficient of compressibility (or the pressure coefficient of thermal expansion). The method proved not to be sensitive enough, however, and after some experimenting I abandoned the attempt to get this sort of information out of the measurements. The blank run was made with tungsten and lead instead of iron and lead as usual. The compressibility of tungsten is less than that of iron, and for this reason it is ideally a better material for the differential measurements. But the second degree term in my previous measurements for tungsten⁶ is perhaps not quite as certain as for iron, so that extrapolation from 12,000 to 50,000 is more hazardous. The compressibility of potassium is so high, however, that there should be no appreciable error here.

The results are shown in Table I. The value at 5,000 was made to agree with the former measurements. At 10,000 and 20,000 the present values of compression are 0.183 and 0.268 respectively against 0.189 and 0.277 found formerly.⁷

Rubidium. Runs were made with two different set-ups; with the second set-up six different runs were made at temperatures between 0° and 75°. The important point at issue was whether rubidium has a transition like that which had just been found for caesium. At first, slight irregularities were found which were favorable to the interpretation of a small transition, but nothing was found that would definitely repeat, and I do not believe that there is a transition up to 45,000 with a volume change as large as 0.00015 cm³/gm.

The two different set-ups gave fairly concordant results for the compression, the greatest discrepancy being at 45,000, where the results were 0.433 and 0.428. The mean results of the two set-ups are given in Table I. The compression at 5,000 was adjusted to agree with the former value⁸ at 50°, this being the only temperature at which measurements had been previously made. The present values for the compressions at 10,000 and 15,000 are 0.233 and 0.279 respectively, against 0.234 and 0.279 formerly.

Caesium. Runs were made with a single set-up at room temperature. Caesium has a fairly small but perfectly clean cut transition at 23,000 kg/cm². At room temperature the transition pressure reached from above and below was not appreciably different. The mean change of volume differed by only 2 per cent from that with either increasing or decreasing pressure, namely 0.0064 cm³ per 1.88 gm, or 0.0034 cm³/gm. (1.88 is the density under standard conditions).

The results are given in Table I. Previous measurements⁹ to 15,000 were made only at 50°, so there is no exact basis for comparison. Present values for ΔV per 1.88 gm at 5,000, 10,000, and 15,000 are 0.182, 0.271, and 0.326 respectively against 0.184, 0.269, and 0.328 formerly. The present value at 5,000 was adjusted to agree with my estimate of what the previous value would have been corrected to room temperature. The transition pressure has also been determined by the discontinuity in resistance; the value found in this way was 22,000 against 23,000 above.

Calcium. The material was some on which I had made compressibility measurements many years ago,¹⁰ probably, although not certainly, from the General Electric Co. It is not as pure as other material from the same source on which I have recently made resistance measurements, or as another sample formerly used also for compressibility.

Runs were made with a single set-up at room temperature, 75°, and 125°. Runs were made at different temperatures in the search for a transition, which had been suggested by previous measurements of shearing strength;¹¹ in fact, the shearing measurements suggested two transitions. In this work persistent irregularities of the right character were found both with increasing and decreasing pressure at all three temperatures, and it is highly probable that there are one or more transitions. The total change of volume is of the order of 0.0008 cm³/gm. The pressures of transition are between 25,000 and 36,000; the sensitivity was not great enough to definitely resolve the irregularities, and good results for the variation with temperature were not found. Previous shearing results indicated the mean pressure of the

transition or transitions as 30,000. Recent measurements of the resistance of calcium to 30,000 have shown no discontinuity up to this pressure; there is nothing inconsistent in this with the existence of a transition, because even if the transition exists below 30,000 it might have been suppressed by viscous resistance.

The results are shown in Table II. No attempt is made in the

TABLE II
COMPRESSION OF THE ALKALI EARTH METALS

Pressure kg/cm ²	Compression		
	Calcium cm ³ /1.538 gm	Strontium cm ³ /2.629 gm	Barium cm ³ /3.62 gm
5,000	.031	.047	.045
10,000	.058	.075	.086
15,000	.082	.099	.121
20,000	.103	.122	.159*
25,000	.122	.136	.186
30,000	.139	.155	.209
35,000	.155	.172	.230
40,000	.171	.188	.250
45,000	.188	.204	.269

* Phase change

Table to suggest any transition, but the results are smoothed right across the irregularities. The volume decrements at 5,000, 10,000, and 20,000 of the present work are 0.031, 0.058, and 0.103 respectively. Previous results on the most nearly comparable sample were 0.029, 0.055, and 0.099 respectively. The present values are consistently higher than the old, the discrepancy thus being in the opposite direction from that of the alkali metals. Impurity of strontium or barium in the present sample would account for the direction of discrepancy.

Strontium. The material was from Eimer and Amend, probably not of very high purity, and the same as that used in recent measurements of the resistance to 30,000. Runs were made with a single set-up at three temperatures: room temperature, 75°, and 125°. The runs were made on the one minute, 2,000 kg schedule. There is quite unmistakably a transition at all three temperatures, but it is unusually difficult to start the transition, the pressures at which the transition starts with increasing and decreasing pressure being separated by an unusually large amount. Furthermore, when the transition starts it

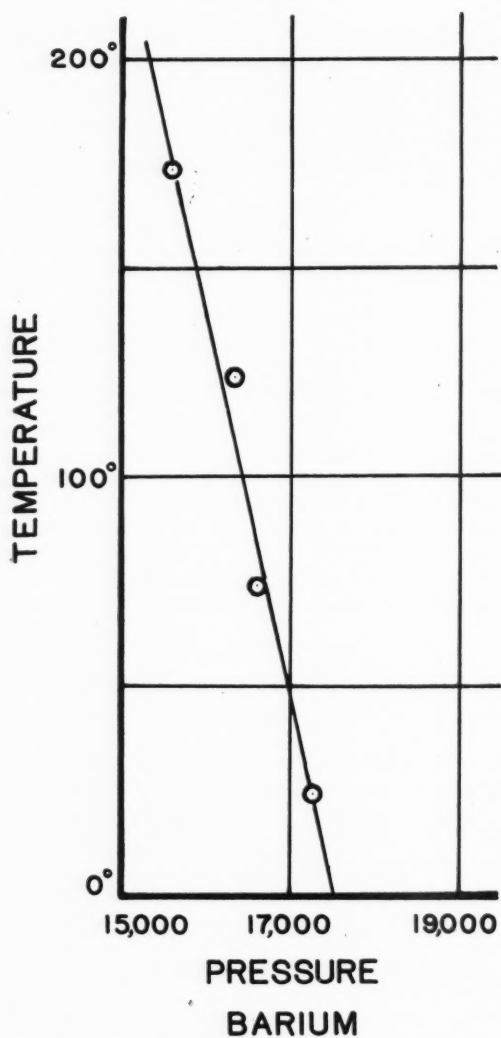


FIGURE 3. Shows the transition temperatures of barium as a function of pressure in kg/cm².

runs very sluggishly, so that with the time schedule employed the transition is running through an unusually wide pressure interval. At the three temperatures, 25°, 75°, and 125°, the respective pressures at which the transition started with increasing pressure was 38,000, 34,000, and 33,000, and with decreasing pressure the corresponding pressures were: 19,000, 19,000, and 18,000. The mean change of volume is 0.0034 cm³/gm, or fractionally 0.0091 on the initial volume. The measured change of volume was less on increasing pressure than on decreasing, which means that the high pressure phase is more compressible than the low pressure phase, the normal direction of

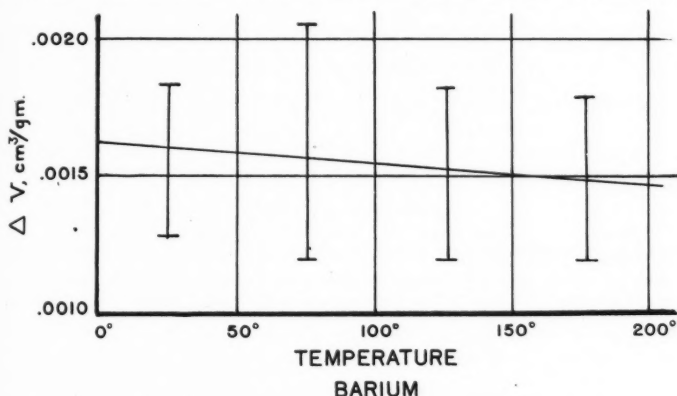


FIGURE 4. The volume changes when barium undergoes transition as a function of temperature along the transition line.

difference. The difference of compressibility is such that in the pressure interval from 17,000 to 43,000 the high pressure phase is compressed by 0.0066 more than the low pressure phase.

The compressions of the low pressure phase are given in Table II; above the pressure of the transition the values are extrapolated with the help of the measured volumes of the high pressure phase. The data already given for the transition may be made to yield the volumes of the high pressure phase above the transition point. The compression at 10,000 was adjusted to agree with the former value.¹² After making this adjustment, the volume at 5,000 is not in at all good agreement with the previous value, ΔV being 0.047 against 0.039 formerly. There is no reason to suspect, however, that this means that the high pressure values are any less reliable than usual.

Barium. The material was from Mackay, and was the same as that used in recent measurements of the resistance to 30,000. Runs were made with a single set-up, and at room temperature, 75° twice, 125°, and 175°. Barium has a perfectly definite transition, running much more sharply and within much narrower pressure limits than strontium. A previous attempt to find a transition of barium with the volumetric apparatus had given negative results;¹³ the apparatus has since been very much improved. The transition pressures and temperatures are shown in Figure 3, the change of volume in Figure 4, and the transition parameters in Table III.

TABLE III
TRANSITION PARAMETERS OF BARIUM

Pressure kg/cm ²	Temperature	$\frac{d\tau}{dp}$	ΔV cm ³ /gm	Latent Heat	
				kg cm/gm	gm cal/gm
17,500	0°	-0.0908	.00163	4.90	.115
16,400	100°	-0.0908	.00155	6.37	.150
15,300	200°	-0.0908	.00147	7.65	.180

The compressions are given in Table II, the low pressure phase below 15,000, and the high pressure phase above. The compression was adjusted to agree with the former value¹⁴ at 5,000. The present values at 10,000 and 15,000 are 0.088 and 0.124 respectively, against 0.089 and 0.124, good agreement.

Indium. The material was inherited from Professor T. W. Richards, and was of high purity. Runs were made with a single set-up at room temperature, 75°, and 125°. There were persistent irregularities at all temperatures that probably mean two or three small transitions; the highest transition pressure is probably in the neighborhood of 40,000, and the lowest around 30,000. The change of volume of the largest transition is probably not more than 0.0002 cm³/gm, with the others not more than half this.

The volume compressions are given in Table IV; no adjustment was made in any of the low pressure values. For comparison there is only a measurement by Richards¹⁵ at pressures up to 500 kg/cm², who found 0.0₂₇ for the initial compressibility, consistent enough with the present values.

Tin. Runs were made with a single filling at room temperature, 100°, and 125°. Previous measurements of shearing¹⁶ suggested a transition, but previous measurements in the volumetric apparatus¹⁷ had given negative results. The volume apparatus was now so much

improved that it seemed worth while to repeat the exploration, but no satisfactory evidence of a transition was found.

The compressions are given in Table IV. No adjustment of values was made at low pressures. The present compressions at 5,000, 10,000, and 20,000 are 0.010, 0.020, and 0.038 respectively, against 0.009, 0.017, and 0.032 former¹⁸ (the last value extrapolated with the second degree formula). The shape of the volume curve is thus somewhat different from that found before. The compressibility of tin is so small that the method is becoming incapable of such relatively accurate results as for most other substances; there is no question but that the previous lower values are to be preferred.

Lead. The measurements on this have already been described in connection with the blank runs. The compressions in terms of the initial volume (that is, cm^3 per 11.35 gm) are given in Table IV.

TABLE IV
COMPRESSION OF FOUR MISCELLANEOUS ELEMENTS

Pressure kg/cm ²	Compressions			
	Indium ^f cm ³ /7.43 gm	Tin cm ³ /7.30 gm	Lead cm ³ /11.35 gm	Sulfur cm ³ /2.07 gm
5,000	.012	.010	.012	.049
10,000	.024	.020	.023	.084
15,000	.035	.029	.032	.110
20,000	.045	.038	.041	.131
25,000	.054	.048	.050	.148
30,000	.064	.057	.058	.162
35,000	.073	.066	.065	.175
40,000	.082 ₅	.075	.072	.186
45,000	.091	.084 ₆	.079	.195

Sulfur. Runs were made with a single set-up at room temperature and 125°. Previous attempts to find a transition had been negative;¹⁹ the present measurements were made with the idea that perhaps with the improved apparatus a transition would now be found. There were irregularities in the neighborhood of 25,000 such as to make a transition not impossible, but I regard it as improbable. If there is one, its ΔV is not more than 0.0003 cm^3/gm .

The values of the compression are given in Table IV. Previously I have made measurements on the linear compressibility in different directions of the single crystal up to 12,000, from which the volume compression may be computed. Agreement with the present values

is exact to two significant figures; the usual adjustment of the low pressure values to secure agreement at some point was not made.

Carbon Dioxide. Measurements were made on this because of the desire of Dr. H. Sponer to secure experimental values of compression with which to check some theoretical calculations.²⁰ Runs were made with a single set-up: two at solid CO_2 temperature, one at 0° , and one at room temperature. The apparatus was filled at liquid air temperature, and an initial pressure of 10,000 kg/cm^2 was applied at this temperature in order to get the CO_2 into a region where it would not leak at higher temperatures. The first application of pressure at solid CO_2 temperature seemed to go without any hitch, but after this there was internal evidence that there may have been slight leak at two or three places. The blank run from which the differential compressibility was determined was made at room temperature; at solid CO_2 temperature the friction of the external surface of the cone is

TABLE V
COMPRESSION OF TWO COMPOUNDS
Compressions

Pressure kg/cm^2	CO_2 Fractional	Na Cl $\text{cm}^3/2.18 \text{ gm}$
5,000	.091	.020
10,000	.142	.037
15,000	.177	.052
20,000	.206	.066
25,000	.226	.078
30,000	.246	.089
35,000	.262	.099
40,000		.108
45,000		.118

much greater than at room temperature, so that there is possibly an error from this factor as well as from the difference of temperature. Furthermore, it was not feasible to determine the quantity of CO_2 by weighing as usual, but it had to be found from measurements of the initial volume. There are several factors, therefore, making the accuracy of these measurements less than usual, but the absolute compressibility of CO_2 is high, and since apparently there are no previous measurements at all, it seemed to me that the rough measurements were worth while.

The numerical values of compression are given in Table V. These run to only 35,000 kg/cm^2 . There is no doubt that at high pressures,

25,000 or higher, there is a transition. This runs sluggishly, and is spread over a considerable pressure range. The fractional ΔV may be as high as 0.003, or perhaps even higher. In view of the various uncertainties, I did not feel justified in attempting to force the results to give the compression of the high pressure phase above 35,000.

Sodium Chloride. Runs were made with a single set-up, at room temperature only. Previous explorations²¹ had made it pretty certain that there is no transition up to nearly 50,000, so that runs at other temperatures were not necessary.

The compressions are given in Table V. The value at 5,000 was adjusted to agree with the previous value²² obtained when making measurements to 12,000. The present values at 10,000 and 20,000 are: 0.037 and 0.066 respectively, against 0.037 and 0.064, the latter value being extrapolated by the second degree formula. The agreement at 10,000 is exact, and at 20,000 the difference is in the direction to be expected in view of the fact that the second degree formula which fits the results to 12,000 gives a minimum in volume at 41,000.

DISCUSSION

The methods of wave mechanics are now so far advanced that it is possible to make fairly satisfactory calculations of compressibilities, at least for the simpler substances. The value of any check of the calculations against experiment is greater the greater the range of the volume change that can be covered by experiment, so that these results should prove particularly useful in giving an idea of the relative importance of the various effects considered by the theory. Theoretical calculations of this sort have been made by Dr. J. Bardeen, and are now in course of preparation for publication. In the case of the alkali metals it is possible to obtain rather good agreement with experiment over the entire range; the agreement is best for caesium, and becomes less good as one moves toward lithium. It turns out that by far the greater part of the compression of caesium is a phenomenon involving the ionic forces in the metal, which are comparatively easy to compute, whereas as one proceeds towards lithium, the electronic interaction terms, which are more difficult to compute, become more important. I shall not attempt myself to go further into the theoretical significance of the results.

There is, however, one matter of a more empirical nature which is of interest. Recently Murnaghan²³ has modified the classical theory of elasticity in such a way that it is capable of dealing rigorously with the relation between stress and strain for finite strain. Of course

when the functional relation between stress and strain is written out explicitly for any particular substance it is not possible to avoid the entrance of empirical constants, such as the coefficients of a power series expansion, but even with this limitation it seems that the form of the function which naturally presents itself in Murnaghan's analysis is better adapted to represent the relation between volume and pressure than many formulas which have been previously used, and therefore is more desirable if short range extrapolation has to be made. Murnaghan's relation between pressure and volume for those cases where two empirical constants are necessary is:

$$p = af + bf^2,$$

where $f = \frac{1}{2} \{ (V_0/V)^{\frac{2}{3}} - 1 \}$, and a and b are constants to be determined empirically.

This formula may be checked as an extrapolation formula. I have made the calculations for caesium, lithium, and sulfur. The tables already given enable f to be determined as a function of pressure. Then a and b were determined so as to agree with experiment at 10,000 and 20,000 kg/cm². The value of f at 45,000 was then substituted into the formula, and the corresponding value of p calculated. Perfect agreement would demand that the calculated p be 45,000. The values actually found were: 44,992, 45,320, and 48,870 respectively for caesium, lithium, and sulfur. The agreement is astonishingly good for caesium and lithium, and still much better than I had expected for sulfur. Murnaghan's formula should, therefore, have much usefulness. I think, however, that too much theoretical significance cannot be attached to the success of the formula. The constants a and b have evidently only an empirical significance, and in fact a and b may have the same or opposite signs in order to fit the experimental points at 10,000 and 20,000. It seems probable to me that the formula in large part owes its success to its mathematical form, which is such that the volume goes to zero when pressure goes to infinity. Many of the equations of state of the past have represented the volume as approaching some finite value at infinite pressure. This is contrary to what we would expect now in the light of our knowledge of the structure of the atom, and is also definitely contrary to the experimental evidence, for the volume at high pressure almost always drops off more rapidly than would be indicated by extrapolation according to the usual formulas from experimental values at low pressures. This would suggest, therefore, that any extrapolation formula giving

zero volume at infinite pressure would have a fair chance of success. I have tried a simple formula of this type for caesium, namely:

$$p = a (V_o/V - 1) + b(V_o/V - 1)^2.$$

If a and b are determined to agree with experiment at 10,000 and 20,000 and are then used in extrapolating, p calculates to 43,300 where it should be 45,000, not bad agreement.

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RESEARCH LABORATORY OF PHYSICS,

HARVARD UNIVERSITY, CAMBRIDGE, MASS.

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1. The first part of the paper is devoted to a general discussion of the problem of the origin of life.

2. The second part of the paper is devoted to a detailed study of the chemical evolution of life.

3. The third part of the paper is devoted to a study of the biological evolution of life.

4. The fourth part of the paper is devoted to a study of the geological evolution of life.

5. The fifth part of the paper is devoted to a study of the historical evolution of life.

6. The sixth part of the paper is devoted to a study of the future evolution of life.

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13. The thirteenth part of the paper is devoted to a study of the economic evolution of life.

14. The fourteenth part of the paper is devoted to a study of the legal evolution of life.

